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THE THERMAL CONDUCTIVITY OF PURE WATER AND STANDARD SEA WATER AS A FUNCTION OF PRESSURE AND TEMPERATURE. PART II. PURE WATER

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Naval Ship Research and Development Center
Annapolis, Maryland

October 1972

NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Md. 20034

THE THERMAL CONDUCTIVITY OF PURE WATER AND STANDARD
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PART II - PURE WATER

by
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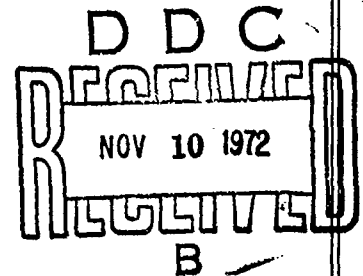
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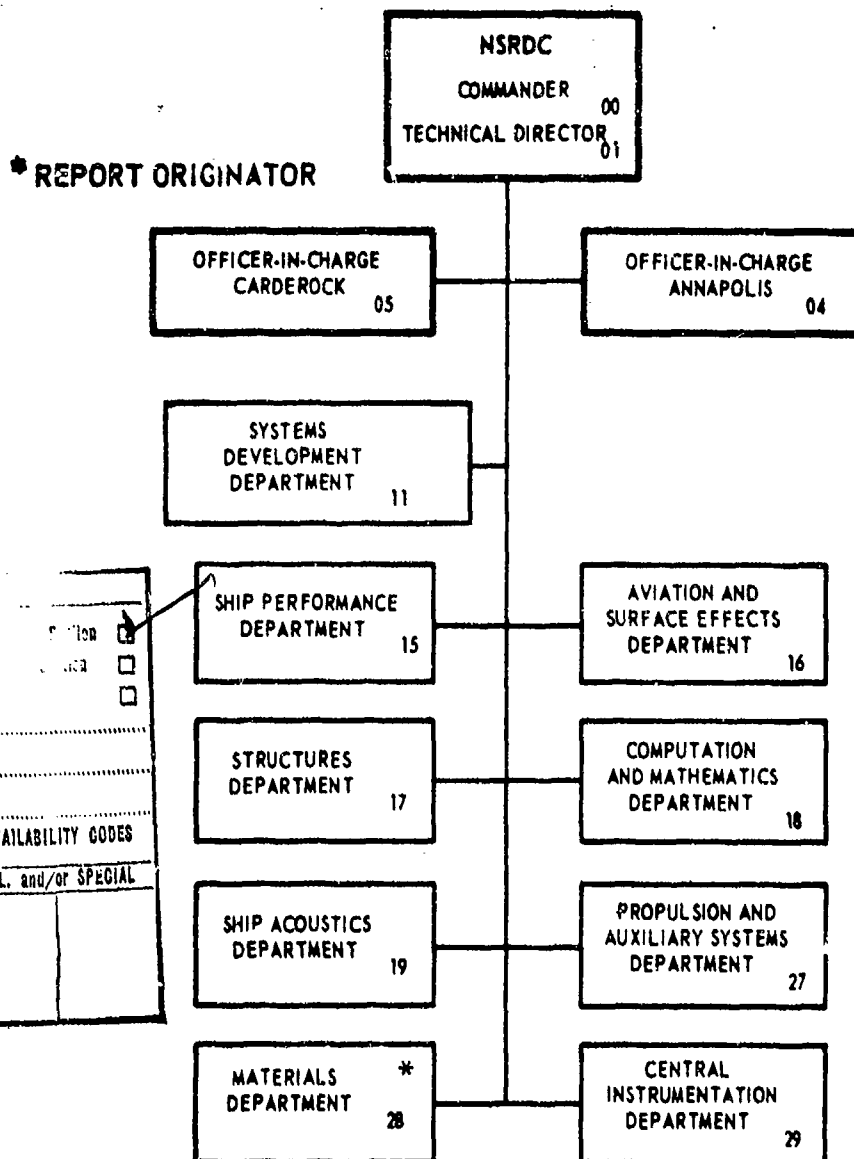### RESEARCH AND DEVELOPMENT REPORT

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INTRODUCTION

A continuing part of the oceanographic research at this laboratory is the determination of the physical and chemical properties of sea water and water at pressure. Projects previously completed have included viscosity and refractive index measurements at pressure. Most recently, measurements of the thermal conductivity of sea water and pure water have been completed in the temperature range of 0°-30° C* and the pressure range of 0-1400 bars. This report is the second part of a series and describes the results of the experimental measurements of the thermal conductivity of pure water.

EXPERIMENTAL INVESTIGATION

Determinations of the thermal conductivity of pure water were conducted for temperatures of +1.83°, 1.86°, 10.32°, 11.68°, 20.28°, 21.76°, 30.28°, and 31.70° C, and nominal pressures of 10, 25, 200, 400, 600, 800, 1000, 1200, and 1400 bars.

The cleaning, filling, and experimental setup and procedures for the use of the special high-pressure vessel have been previously described.[1] The water used for these measurements was freshly distilled and deionized, with a specific conductance of 0.47 micromhos/cm. The purity of the water was not judged to be extremely critical on the basis of Riedel's[2] findings which showed minimal effects for salt in aqueous solution.

PRECISION, ACCURACY, AND ERROR ANALYSIS

Two distinct series of measurements were conducted by utilizing different thermocouple junctions. Each series consisted of at least three determinations of each data point and many determinations of selected "reference" data points, primarily at 10 and 25 bars pressure. In almost all cases, the data resulting from any particular series agrees to within 0.2% of the mean value. This small variation was traced to the procedure used to measure the temperature differential. The setup required solder joints to mate the thermocouple leads to the high-pressure electrical feedthroughs.[1] These joints required unsoldering and resoldering during each assembly of the apparatus. This was observed to cause a variation in the thermocouple electromotive force (EMF) of 0.5 µv, which is ±0.2% of the approximately 130-150 µv generated by the temperature gradient. The accuracy of thermocouple differential temperature measurement can only be estimated and is thought to be ±0.5%, based upon comparison of the results

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*Abbreviations used in this text are from the GPO Style Manual, 1967, unless otherwise noted.
[1]Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

obtained with both sets of thermocouples. This estimate is believed to be conservative because of the short temperature differential (<1.0° C) and because the increase of the EMF/degree is not rapid. The EMF values used to calibrate the thermocouples and generate the least squares 10th degree interpolation poly-nomial were obtained from the National Bureau of Standards. These values will be incorporated into a new circular, as yet unpublished, which supercedes NBS circular 561.

The temperature bath around the pressure vessel was controlled to ±0.01° C and measured with a quartz crystal thermometer with an absolute accuracy (after ice point calibration) of ±0.05° C. An error of ±0.05° C in this measurement results in an inaccuracy of ±0.02% in K, the thermal conductivity constant.

The pressure was measured with Heise pressure gages that were calibrated to ±0.1%. A variation of ±0.1% would result in an error in K of ±0.06%.

The power measurement consisted of independent determinations of both voltage and current. The minimum accuracy of the voltage measurement is ±0.06%, while that for current is ±0.12%.

The measurements used to deduce the cell constant[1] contribute an error of ±0.18% based upon a maximum measurement error of ±7 parts in 100,000.

Finally, heat-loss errors which were kept to a minimum through design are estimated to result in an error of ±0.1%.

The total error for which corrections cannot be applied is therefore calculated to be ±1.04%, or between 5.5×10^{-5} and 6.5×10^{-5} watts/cm-degree, depending upon the value of K.

The single error for which correction of experimental results is possible is concerned with the placement of the thermocouple probes. Through design limitations, thermocouples could not be placed directly at the surface of the liquid. This finite distance contributed errors of from 1.35% to 1.60%, depending upon the value of K which changed in relation to temperature and pressure of the fluid. In all calculations, the thermal conductivity of silver, K_s, was taken as a constant with respect to pressure and temperature at 4.209 watts/cm-degree; d_1, the average distance between the three inner probes and the inner surface of the liquid, equal to 0.210 cm (0.083 inch); and d_2, the average distance between the outer probes and the outer surface of the liquid, equal to 0.292 cm (0.115 inch). The actual calculation of K for the liquid was accomplished using the formula:

$$2\pi L \, \Delta T = V \, I \left[\frac{\ln \frac{r_c}{r_o - d_1}}{K_s} + \frac{\ln \frac{r}{r_o}}{K} + \frac{\ln \frac{r}{r + d_2}}{K_s} \right], \qquad (1)$$

where

L = length of thermally conductive fluid path

ΔT = total temperature drop observed experimentally

V = voltage drop across the heater

I = current through the heater

r_o = internal radius of fluid annulus

r = external radius of fluid annulus

K = thermal conductivity of fluid

K_s = thermal conductivity of silver

d_1 = distance from inner thermocouples to inner surface of fluid

d_2 = distance from outer thermocouples to outer surface of fluid.

RESULTS

The corrected experimental results of the measurements are listed in table 1 and shown graphically in figure 1.

TABLE 1
THERMAL CONDUCTIVITY (10^{-5} WATTS/CM-DEGREE) FOR TEMPERATURES
OF 1.83°-31.70° C AND PRESSURES TO 1400 BARS AS MEASURED
BY IRON- AND CHROMEL-CONSTANTAN THERMOCOUPLES

Gage Pressure bars	$K^{(1)}$				$K^{(2)}$			
	Temperature, ° C							
	1.83	10.32	20.28	30.26	1.66	11.66	21.76	31.70
10	563.0	580.5	597.0	611.0	-	-	-	-
25	-	-	-	-	560.0	581.0	596.5	611.0
200	572.0	588.0	605.0	618.0	566.0	589.5	604.0	619.0
400	580.5	597.5	613.5	627.5	577.5	596.5	611.5	627.0
600	589.0	606.0	622.0	635.0	585.5	607.0	621.0	635.5
800	597.0	614.0	630.5	643.5	594.5	615.5	628.5	643.5
1000	604.0	623.5	638.0	653.0	604.0	622.0	639.0	652.0
1200	612.0	630.0	647.0	659.5	613.0	632.0	648.5	660.5
1400	(3)	639.5	654.5	668.5	(3)	642.0	655.5	669.0

(1) Measured by Iron - Constantan thermocouple junctions.
(2) Measured by Chromel - Constantan thermocouple junctions.
(3) Leaking seals - no reading taken.

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The data can be represented as a function of temperature and pressure by the equation:

$$K = 5.5780 \times 10^{-3} + 4.249 \times 10^{-7} P + 2.223 \times 10^{-5} T - 1.797 \times 10^{-7} T^2, \qquad (2)$$

where K is given in watts/cm-degree, P is the pressure in bars, and T is the temperature in ° C. The values generated by this equation are given in table 2 and shown graphically in figure 2. These have a standard error of ±1.5 x 10^{-5} watts/cm-degree, or ±0.25% from the experimental data.

TABLE 2
VALUES OF THE THERMAL CONDUCTIVITY (10^{-5} WATTS/CM-DEGREE)
OF PURE WATER, AS DETERMINED FROM EQUATION (2)

Gage Pressure bars	Temperature, ° C			
	0	10	20	30
0	557.5	578.5	595.0	608.5
200	565.0	586.5	603.5	617.0
400	574.5	595.0	612.0	625.5
600	583.0	603.5	620.5	634.0
800	591.5	612.0	629.0	642.5
1000	600.0	620.5	637.5	650.5
1200	608.5	629.0	646.0	659.0
1400	617.0	637.5	654.5	667.5

DISCUSSION

Direct comparison of the data in table 2 with that reported in the literature is only partly possible because most data for high pressure covers higher temperature ranges, and that for lower temperatures is restricted to low pressures.

Powell's[3] review and analysis of all the atmospheric pressure determinations has resulted in a set of "most probable" values for water. These data are shown in figure 3 in comparison to our atmospheric values, as determined from equation (1). It can be seen that our results are systematically about 0.5%-1% lower than those "most probable" values cited by Powell. While the origin of this discrepancy is unknown, no special effort was made to resolve this difference since we are primarily concerned with the effect of pressure on the thermal conductivity.

Previous determinations of the thermal conductivity of water at high pressure have been conducted by Bridgeman,[4] Lawson, et al.,[5] and Timrot and Vargaftik;[6] however, the overlap with our data is sparce. Figure 4 shows the data of Bridgeman (corrected in accordance with the recommendations of Riedel[7]), Lawson, et al., and our results for a temperature of 30° C. All results agree closely with slopes of 3.7×10^{-7}, 3.9×10^{-7}, and 4.2×10^{-7} watts/cm-degree-bar, respectively. In addition, our absolute results are in excellent agreement (±0.5%) with those given by Lawson.

The data obtained by Timrot and Vargaftik for 0° C for pressures to 400 atmospheres appear in figure 5, along with ours for the same temperature. Both sets of results agree within 1% of each absolutely, with slopes of 4.1×10^{-7} and 4.2×10^{-7} watts/cm-degree-bar, respectively.

THEORETICAL RELATIONSHIPS

Relationships between thermal conductivity and other physically measurable quantities have been advanced on the basis of both empirical and theoretical groundwork.

One of the earliest relationships known was that proposed by Weber.[8] He introduced an empirical formula which was later theoretically deduced by Predvoditelev,[9] and relates density (ρ), specific heat at constant pressure (C_p), and molecular weight (m), and the thermal conductivity (K), to a constant (A). The formula is:

$$\frac{K}{C_p} \left(\frac{m}{\rho} \right)^{1/3} = A. \tag{3}$$

The value of this constant as computed from our conductivity data, and values of C_p and ρ as taken from the literature,[10] can be seen in table 3 for pressures up to 1000 bars. It is evident that this equation is not valid for the pure water system.

Another relationship is that given by Bridgeman,[4] relating the thermal conductivity (K), to the density (ρ), the absolute weight of a molecule (m), the velocity of sound in the medium (v), and the Boltzman gas constant (k), by

$$K = 2kv \left(\frac{\rho}{m} \right)^{2/3}. \tag{4}$$

TABLE 3
VALUES OF THE CONSTANT A AS DETERMINED FROM WEBER'S FORMULA

Gage Pressure bars	Temperature, ° C			
	0	10	20	30
0	346.6	361.9	373.9	384.0
200	355.0	368.5	380.0	389.5
400	362.7	374.8	385.5	394.6
600	369.9	380.6	390.6	399.3
800	376.5	385.9	395.3	403.7
1000	382.7	390.9	399.6	407.5

However, this relationship yields values of K only about two thirds of the experimental values for thermal conductivity. Bridgeman's value of 2.02×10^{-16} ergs/degree for the Boltzman gas constant, k, is in error by almost 50% and accounts for the rather close agreement between his calculated and experimental values. This equation, when quoted by El'Darov,[10] is given in the slightly different form of

$$K = 3kv \left(\frac{\rho}{m}\right)^{2/3} .$$ (5)

Because of the discrepancy between equations (4) and (5) concerning the value of the constant, we decided to evaluate its magnitude according to our values for the thermal conductivity, such that

$$\frac{K}{kv} \left(\frac{m}{\rho}\right)^{2/3} = B.$$ (6)

Values for B are tabulated at pressures to 1000 bars, the limit of other available data, in table 4. It is obvious from this table that B is constant neither with respect to temperature, nor pressure.

An equation given by Vargaftik[11] expresses the temperature dependence of thermal conductivity of liquids as

$$K = C\rho^{4/3} ,$$ (7)

where K and ρ have their usual meanings, and C is a constant dependent upon pressure. Table 5 gives values of C based upon our experiments. It is again quite evident that this equation is not valid for the pure water system

TABLE 4
VALUES FOR THE CONSTANT B FROM EQUATION (6)

Gage Pressure bars	Temperature, ° C			
	0	10	20	30
0	2.774	2.789	2.803	2.821
200	2.736	2.749	2.766	2.782
400	2.696	2.711	2.729	2.745
600	2.655	2.674	2.693	2.710
800	2.615	2.638	2.659	2.677
1000	2.577	2.603	2.627	2.645

TABLE 5
VALUES FOR THE CONSTANT C IN EQUATION (7)

Gage Pressure bars	Temperature, ° C			
	0	10	20	30
0	179.3	172.8	167.7	163.4
200	179.0	172.6	167.3	163.0
400	178.6	172.1	166.8	162.6
600	178.1	171.6	166.4	162.1
800	177.5	171.1	165.8	161.6
1000	176.8	170.4	165.2	161.2

CONCLUSIONS

● The reported thermal conductivity of pure water is in excellent agreement with historical data thus giving credence to the design and techniques used.

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● Thermal conductivity of pure water is a direct linear function of pressure throughout the pressure and temperature range investigated.

● Previously proposed equations relating thermal conductivity to other measurable bulk properties have failed to accurately describe the pure water system.

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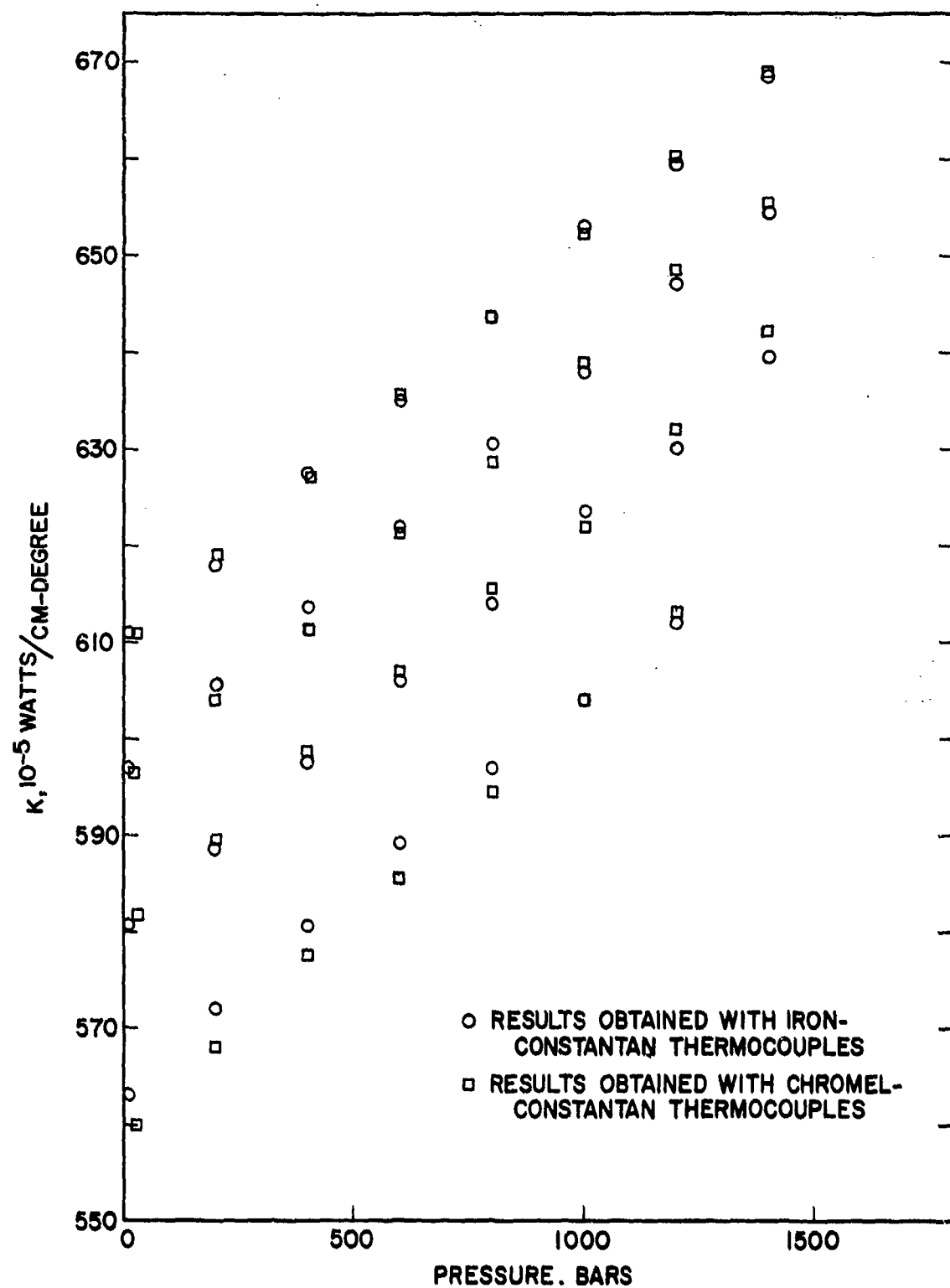11 - Vargaftik, N. B., Thesis, ENIN, USSR Academy of Sciences (1951)

Figure 1

Experimental Data for the Thermal Conductivity
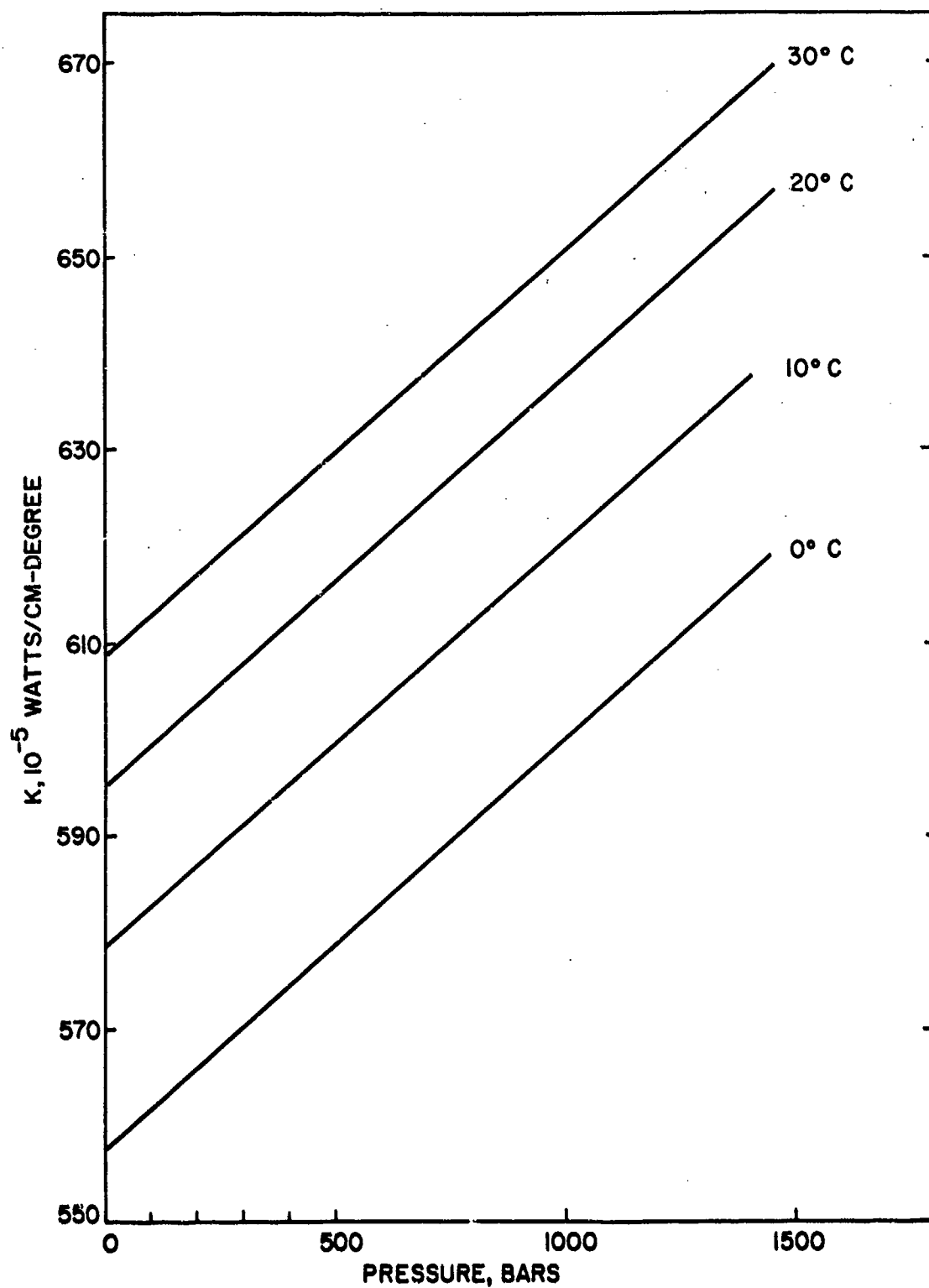of Pure Water as a Function of Pressure for Various Temperatures

Figure 2
Thermal Conductivity of Pure Water as Determined by
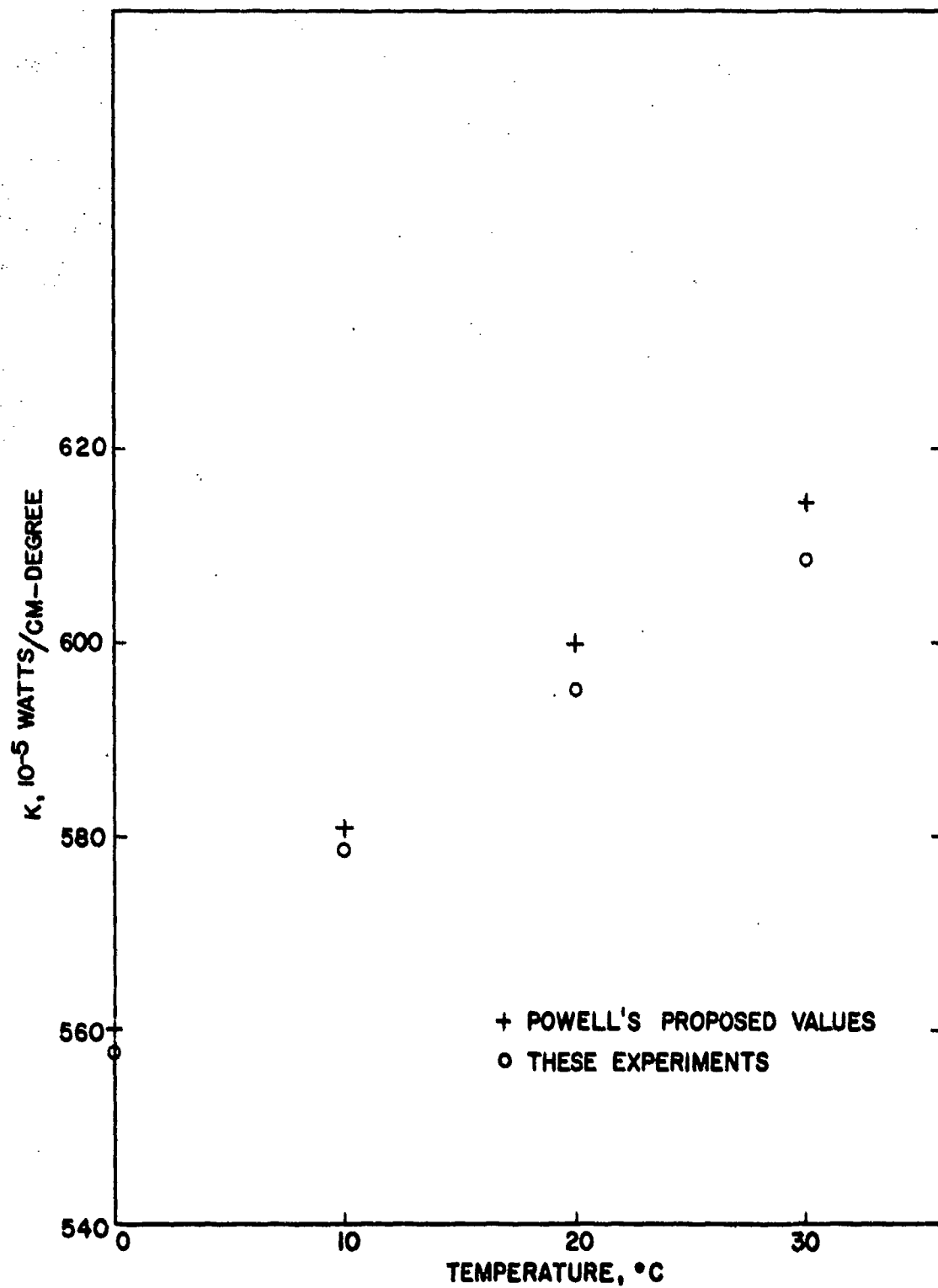Equation of Least Squares for Experimental Data

10.

Figure 3
Comparison of Powell's Proposed Values for
Thermal Conductivity of Pure Water at Atmospheric
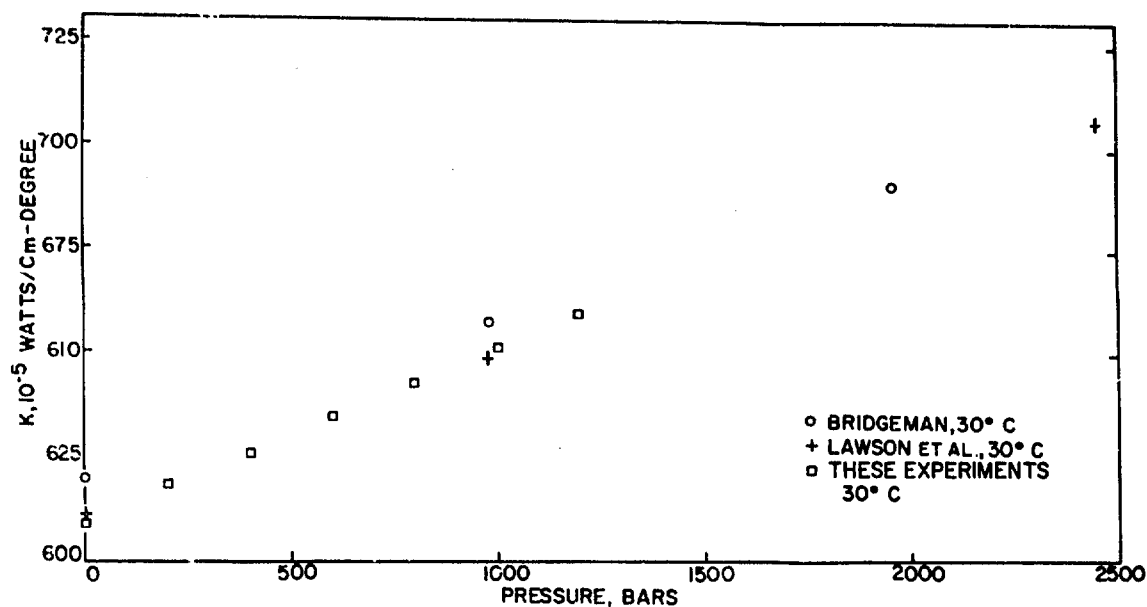Pressure with Results of These Experiments

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Figure 4
Historical Determination of the Effect of Pressure
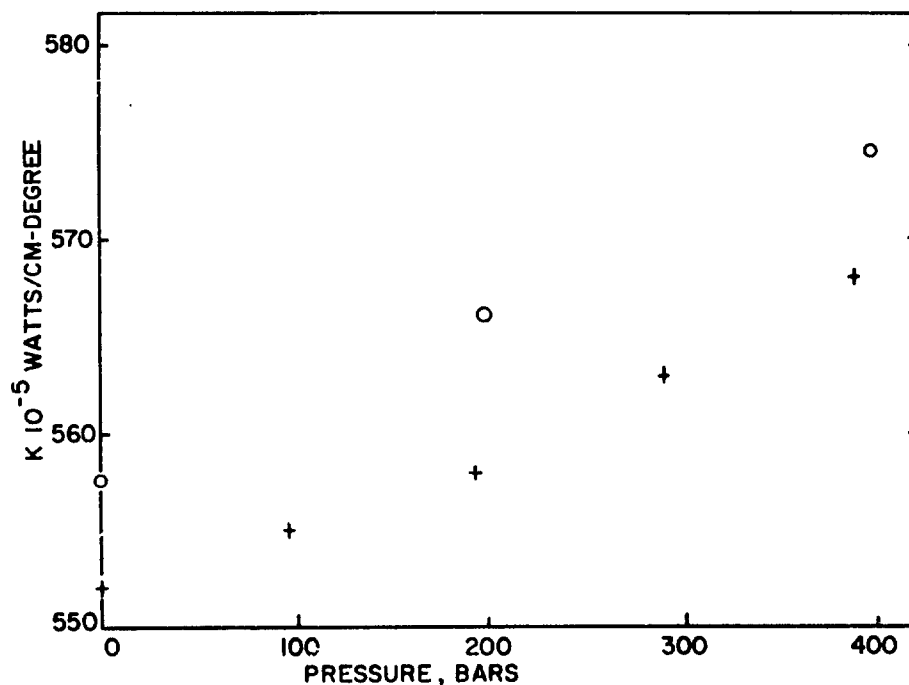on the Thermal Conductivity of Pure Water
for a Temperature of 30° C

Figure 5
Historical Determination of the Effect of Pressure
on the Thermal Conductivity of Pure Water
for a Temperature of 0° C

12.